

**Ruthenium Enhancement in Methanol
Oxidation Electrocatalysis in the Surface
NMR Perspective (Electrochemical NMR)**

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Progress in fuel cell science and technology is one of major steps in securing future energy needs of mankind, and a major future investment into remediation of global climate warming trends that have developed in the past century (Interface, 10, 21-36 (2001); ECS PV, 2000-20). Fuel cells are more efficient than conventional power generation devices and operate free of atmospheric contaminants. Methanol is proposed as fuel in the direct oxidation methanol fuel cell (DMFC). The best catalyst for DMFC is obtained by deposition of platinum/ruthenium nanoparticles on a carbon support or directly on Nafion PEM membranes, with the ruthenium component added to reduce inauspicious methanol self-poisoning that leads to CO chemisorbate formation. This paper will contribute to increasing understanding of ruthenium promotion phenomena on the electronic density of states level.

The foundations of electrochemical NMR, NMR instrumentation and the rf pulse sequence will be covered in the second talk at the present ECS/ISE meeting (A. Wieckowski et al.). In this presentation, we will demonstrate correlations between Allred-Rochow electronegativity of surface ligands and their influences on surface electronic properties of Pt electrodes (as viewed by Pt-195 NMR), and the applicability of Friedel-Heine invariance of LDOS in studies of nanoparticle electrochemical systems. Specifically, we will investigate 10 nm fuel cell grade platinum electrocatalyst covered by ruthenium via the spontaneous deposition method by using electrochemical nuclear magnetic resonance spectroscopy (EC-NMR) in conjunction with potentiodynamic/potentiostatic electrochemistry and radioactive labeling studies. We will show that, in addition to a "bi-functional" mechanism of the CO oxidation, there exist some major cooperative electronic and surface dynamic contributions to the oxidation process. We will conclude that adding ruthenium to the platinum catalyst weakens the Pt-CO bonding, activates water on the surface, and increases the rate of CO surface diffusion to the active Pt/Ru sites.